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TEMPERATURE REGIMES FOR OBTAINING GRANULAR MATERIAL FOR FOAMED CRYSTAL GLASS MATERIALS AS A FUNCTION OF THE BATCH COMPOSITION

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The temperature regimes for obtaining granular glass, which is the initial material for foamed crystal glass materials, are examined as a function of the batch composition and the nature of the main glass-forming component. It is determined that batches based on natural silica- and alumina-containing materials exhibit different behavior when heated. When a batch is processed under the conditions of a commercial conveyor-type furnace, the temperature regime must be tailored to each batch in order to obtain high-quality granular glass.

Key words: foamed glass, mix, granular glass.

At the present time, one of the important problems of manufacturing foam glass is due to limited conventional raw materials base — secondary glass scrap. Previous investigations have shown that it is possible to obtain granular glass — the initial material for foamed crystal glass materials based on different types of common natural and technogenic materials by means of low-temperature (below 900°C) processing of the batch (RF Patent No. 2326841). It has been established that the amount of the glass phase in granular material must be at least 70% to obtain foamed crystal glass and 90% or more to attain low density (to 150 kg/cm³). The strength of the foamed crystal glass materials, which is determined by the amount of the crystal phase and the size of the residual crystals, increases as the crystals decrease to micro- and nanometer sizes. The technological properties of the glass granulate largely depends on the composition and heat-treatment temperature of the initial batch.

The objective of the present work is to determine the dependence of the heat-treatment regime for batches with the maximum amount of the glass phase in the mix on the composition of the initial batches based on silica- and alumina-containing natural materials for the conditions of a pilot conveyor-type furnace.

The temperature regime in the furnace is automatically regulated by heating zones (total length of the zones 4.5 m) and by the velocity of the conveyor belt from 1 to 25 cm/min, for which the average rates of heating of the batch up to 900°C range from 6 to 18 K/min, respectively.

The following materials were used for the main components of the glass batches: marshalite (Elbashenskoe deposit), diatomite, opoka (Inzenskoe deposit), and zeolite (Sakhaptinskoe deposit), whose general properties are presented in [1, 2] and whose chemical composition is presented in Table 1. First, to determine the batch composition basic glass compositions were chosen taking account of the three-component phase diagrams. The computed values of the melting

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TABLE 1.

| Material | Content, wt. % | | | | | | | |
|------------|------------------|--------------------------------|--------------------------------|------|------|-------------------|------------------|--------------------|
| | SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | CaO | MgO | Na ₂ O | K ₂ O | calcination losses |
| Marshalite | 95.70 | 2.10 | 0.27 | 0.80 | 0.60 | — | — | 0.53 |
| Diatomite | 86.44 | 5.30 | 1.60 | 0.74 | 0.53 | — | — | 4.80 |
| Opoka | 83.00 | 5.25 | 2.72 | 2.05 | 1.47 | — | — | 5.90 |
| Zeolite | 63.12 | 13.26 | 2.38 | 3.50 | 1.75 | 1.04 | 3.07 | 11.88 |

TABLE 2.

| Composition | Oxide content in the system, wt. % | Melting temperature, °C | Melt amount, % |
|------------------|--|-------------------------|----------------|
| Silicic | 21Na ₂ O – 5CaO – 74SiO ₂ | 725 | 100 |
| | | (eutectic) | |
| | | 800 | 46 |
| | | 900 | 65 |
| | | 950 | 77 |
| Alumino-silicate | 22Na ₂ O – 4Al ₂ O ₃ – 74SiO ₂ | 1000 | 100 |
| | | 800 | 83 |
| | | 850 | 100 |
| | | 800 | 77 |
| | | 880 | 100 |

temperatures and the amount of melt formed (Table 2) showed that the amount of the liquid phase for which the batch transitions into a liquid-flowing state is attained for aluminosilicate compositions (in the system Na₂O – Al₂O₃ – SiO₂) at temperatures not exceeding 800°C and for silica compositions (in the system Na₂O – CaO – SiO₂) at 950°C (with the exception of the eutectic composition). Complete loss of shape of the granules when the batch transitions into the liquid state can be prevented by heating the batch at a definite rate.

In summary, it is important to tailor an individual heat-treatment regime to each batch taking account of the softening temperature of the batch and the rate of heating, which in conveyor furnaces is regulated by the velocity of the belt. To this end, a method was developed for determining the softening interval of the mix, making it possible to evaluate its behavior during the heating process. The following conditions were satisfied:

the maximum heat-treatment temperature of the batch was 900°C;

the batch was granulated before heat-treatment; this ensures that the spherical granules are heat through uniformly and more quickly and that the higher chemical activity is higher as compared with powdered batch;

the batch must transition gradually into a fused state without the granules being completely destroyed, since a rapid increase of the amount of the liquid phase results in complete spreading and sticking of the granules, which is critical when the process is conducted in conveyor furnaces.

Following the procedure, the softening temperature interval of the batch was determined with a specially manufactured facility that made it possible to record the penetration distance of the rod into the layer of densified batch as the batch softens. The relative penetration Δh of the rod into the batch as the latter is heated can be calculated from the relation

$$\Delta h = [(h_0 - h_1)/h_0] \times 100,$$

where h_0 is the initially recorded height of the sample, mm, and h_1 is the penetration depth of the rod, mm.

TABLE 3.

| Batch | Content, wt. % | | | | | |
|-------|----------------|-----------|-------|---------|------|----------|
| | marshalite | diatomite | opoka | zeolite | soda | dolomite |
| M1 | 63 | – | – | – | 30 | 7 |
| M2 | 63 | – | – | – | 20 | 17 |
| D1 | – | 67 | – | – | 27 | 6 |
| D2 | – | 66 | – | – | 18 | 16 |
| O1 | – | – | 68 | – | 29 | 3 |
| O2 | – | – | 68 | – | 17 | 15 |
| Z3 | 55 | – | – | 17 | 28 | – |
| Z4 | – | – | – | 76 | 24 | – |

The results of the tests performed on the batches based on marshalite (M1, M2), diatomite (D1, D2), opoka (O1, O2), and zeolite (Z3, Z4), whose compositions are given in Table 3, are presented in Fig. 1.

The curves of the variation of the relative penetration into the batch as the batch is heated on the whole do not show strictly determined, regular behavior. However, three characteristic sections differing by the penetration velocity of the rod can be identified in the region corresponding to a transition of the batch from the solid into a viscofluid state. Intense release of gas occurs in the first section; this is due to carbonate decomposition and silicate formation reactions. In the present case the reactions proceed in a solid – gas system and the batch is observed to swell, which is recorded by rising of the rod (negative values of the penetration coefficient). A liquid phase forms at the second stage (solid – gas – liquid system); this causes the rod to drop with different velocity depending on the composition of the batch and, in consequence, with different viscosity of the melt. The third state (rectilinear section of the curve) is characterized by complete fusion of the batch and, subsequently, liquid-phase sintering in the absence of processes associated with gas formation (solid – liquid system).

The temperature interval corresponding to a phase transition of the batch from the solid into a viscofluid state (second section of the curve) plays a considerable role in the processes occurring; it is suggested that the softening interval of the batch be recorded for a comparative evaluation. The batches are divided into two groups depending on the magnitude of the temperature interval: slowly softening ($\Delta t \geq 110^\circ\text{C}$) batches, for which a relatively high rate of increase of the temperature during heat treatment (18 K/min) is recommended, and rapidly softening batches ($\Delta t < 110^\circ\text{C}$), which must be processed slowly (6 K/min), or the composition of the batch must be adjusted by adding components that increase the viscosity of the melt.

The temperature corresponding to the inflection point on the curve of the penetration depth of the rod into the batch versus the heating temperature of the batch was taken as the processing temperature for the batch. The value of this tem-

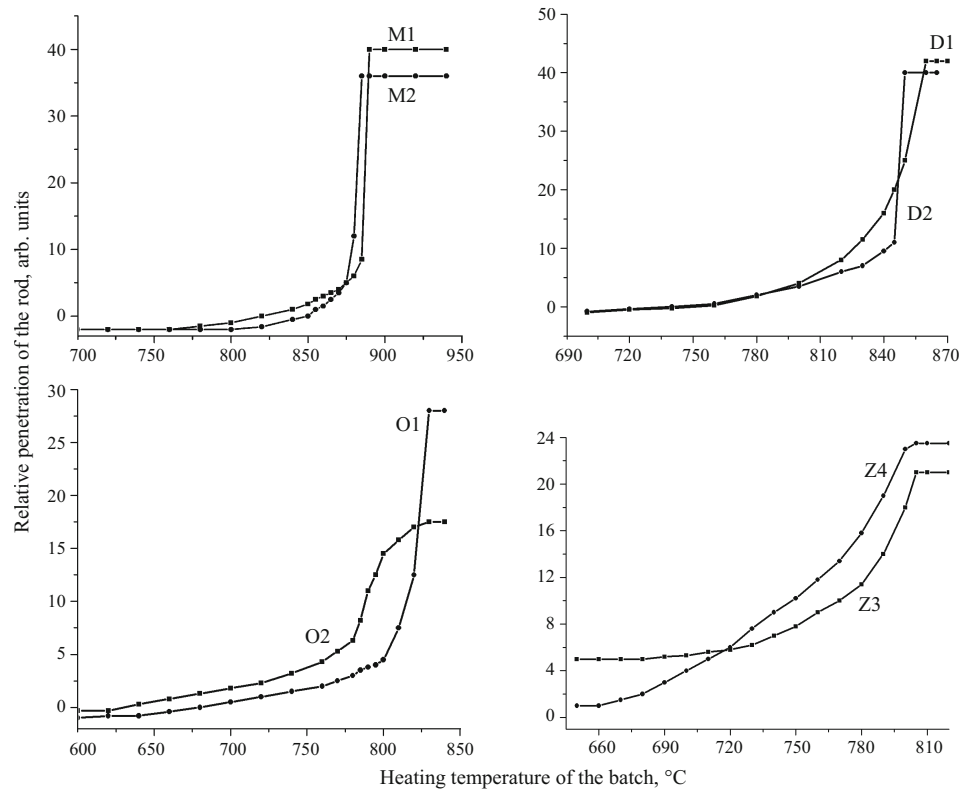


Fig. 1. Penetration of a rod versus the heating temperature of the batch.

perature is found by constructing the curve of the first derivative ($\Delta h/\Delta t$) versus the processing temperature of the batch (Fig. 2). This temperature depends on the composition of the batch and the nature of its main component. For example, in the case of diatomite and opoka the refractory silica is present in an amorphous state; this lowers the softening tempera-

ture of the batch as compared with the marshalite-based batch, containing crystalline SiO_2 .

At higher temperatures the batch transitions into a liquid state, which occurs when the amount of melt more than 70%. Slow heating makes it possible to avoid complete melting of the granules. The greater the amount of liquid phase formed

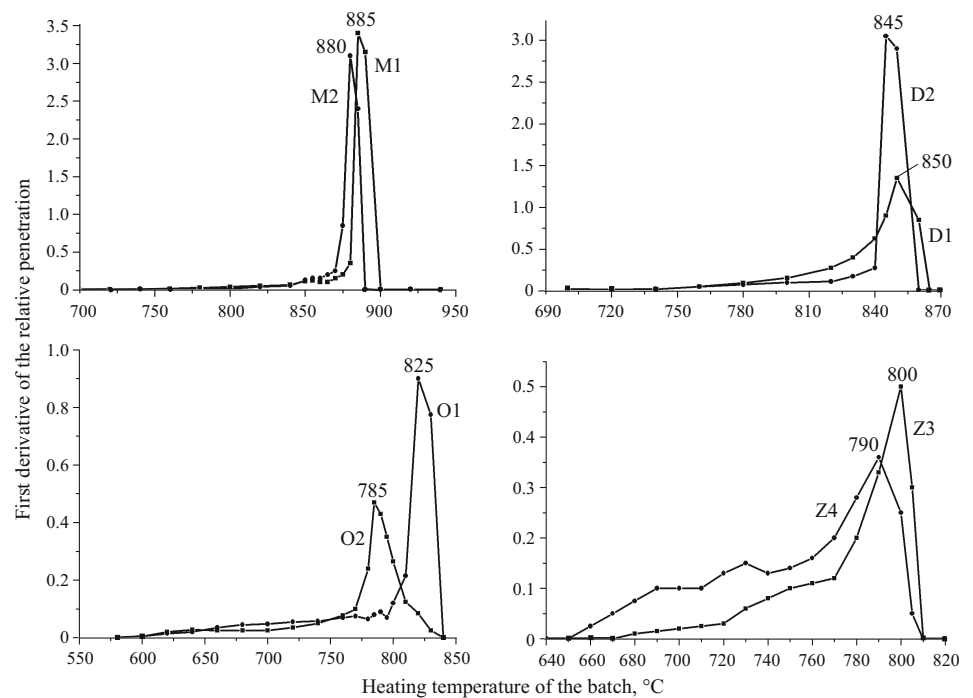


Fig. 2. First derivative $\Delta h/\Delta t$ of the relative penetration versus the heating temperature of the batch.

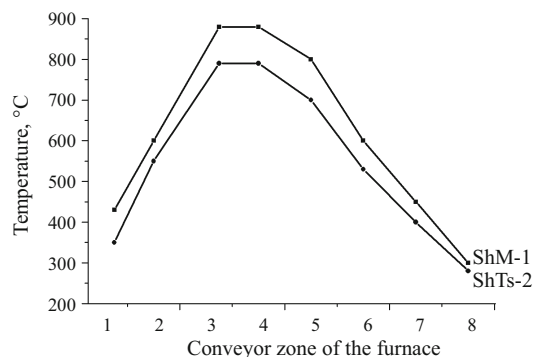


Fig. 3. Process temperature for a batch along the zones of a conveyor furnace.

and the lower the temperature at which it appears, the lower the processing temperature of the batch is.

The processing temperature and rate of heating of the batch were chosen on the basis of the investigations. Accordingly, granular glass material with the corresponding technological properties was obtained on the furnace's conveyor belt. The processing temperatures for the rapidly and slowly softening batches along eight zones of the conveyor furnace are shown in Fig. 3 for a batch with marshalite and zeolite.

The following conclusions can be drawn from the dependences obtained.

The processing temperature of the batches calculated according to the basic composition of glass increases with the amount of SiO_2 and decreases with the impurity content in the silicic component — from 800°C for batches based on zeolite (63% SiO_2) to 885°C for batches with marshalite (95.7% SiO_2).

The softening temperature interval of the batches expands with increasing fraction of the amorphous component

SiO_2 in the silicic component (185°C for opoka-based batch and 85°C for marshalite-based batch).

The batches containing silicic components in a crystalline form (marshalite) belong to the rapidly softening group while batches containing amorphous SiO_2 (diatomite, opoka) belong to the slowly softening group. It is recommended that these batches be heat-treated using relatively slow (6 K/min) and rapid (18 K/min) rates of heating, respectively.

The two-component zeolite-containing batch, which because of the particularities of its internal structure belongs to the slowly softening group, has the lowest softening temperature (790°C). Adding marshalite decreases the softening temperature interval substantially (from 140 to 95°C), which is must be taken into account when choosing the heating rate for batches.

In summary, the temperatures at which batches are heat-treated in order to obtain a granular glass material is largely determined by the composition and nature of its glass-forming component, specifically, the content of SiO_2 and the amount of impurities in the component, the relative amount of amorphous SiO_2 , and the silicic or aluminosilicate composition. The behavioral diversity of batches based on different rocks makes it necessary to determine for each batch separately a processing regime that can be implemented under laboratory conditions.

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